NASA Aeronautics Research Institute

Development of Engineered Ceramic Matrix Composites

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Acknowledgements

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Program Manager: Dr. Koushik Datta (NARI)

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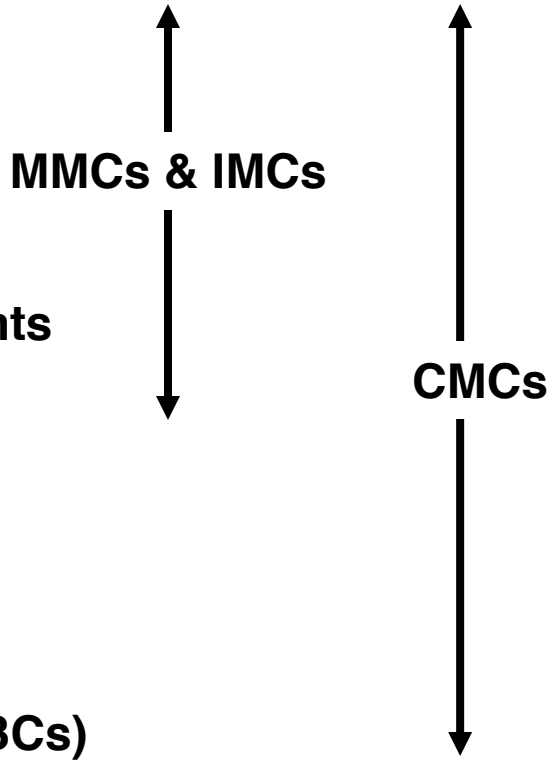
Introduction

- **Advanced aircraft engines require the use of reliable, lightweight, creep-resistant and environmentally durable materials.**
- **Silicon carbide-based ceramic matrix composite (CMC) technology is being developed to replace nickel-based superalloy blades and vanes.**
  - **Near term 1589 K (2400 °F) (cooled).**
  - **Medium term 1755 K (2700 °F) (cooled).**

Factors Affecting Composite Properties

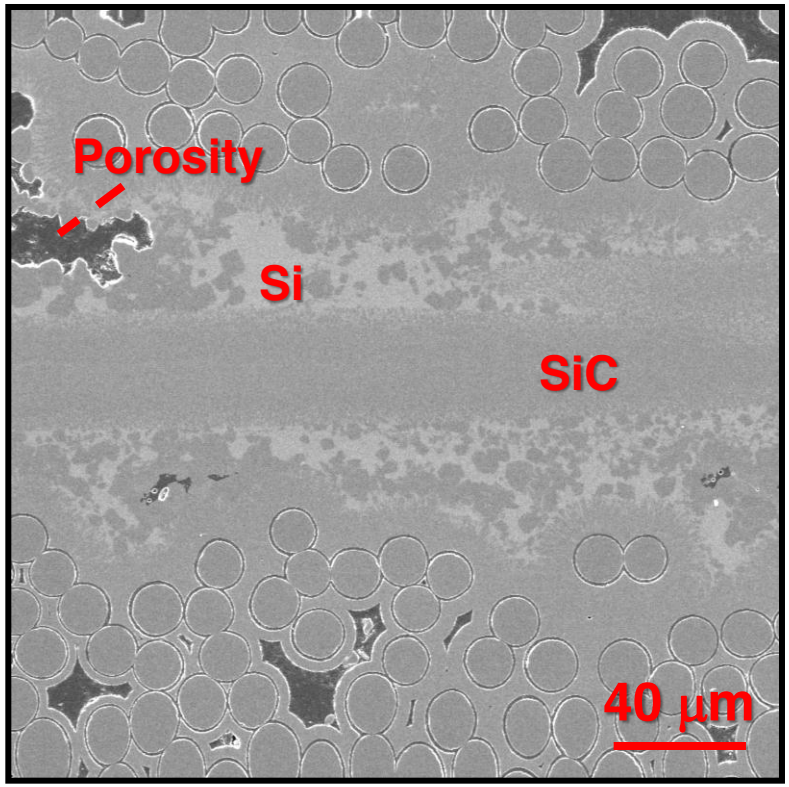
Composites are engineered systems, whose properties depend on:

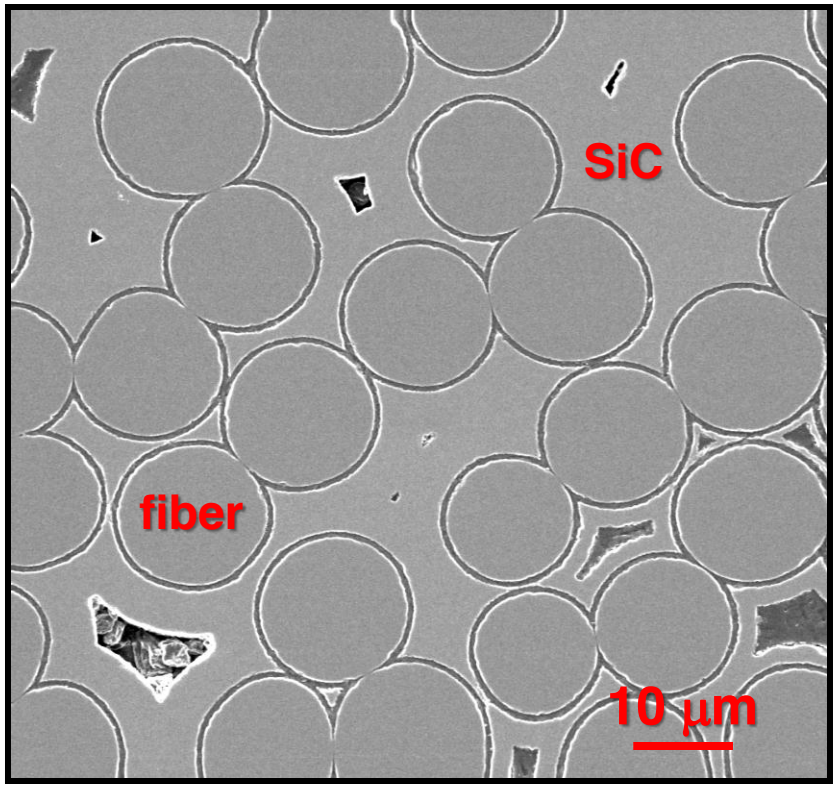
- Fiber properties
- Matrix properties
- Interfacial properties
- Volume fractions of the constituents
- Processing
- Fiber weave architecture
- Fiber coatings
- Protective coatings (e.g. EBCs, TBCs)



Typical Microstructures of As-Processed BN-Coated Hi-Nicalon MI SiC Composites

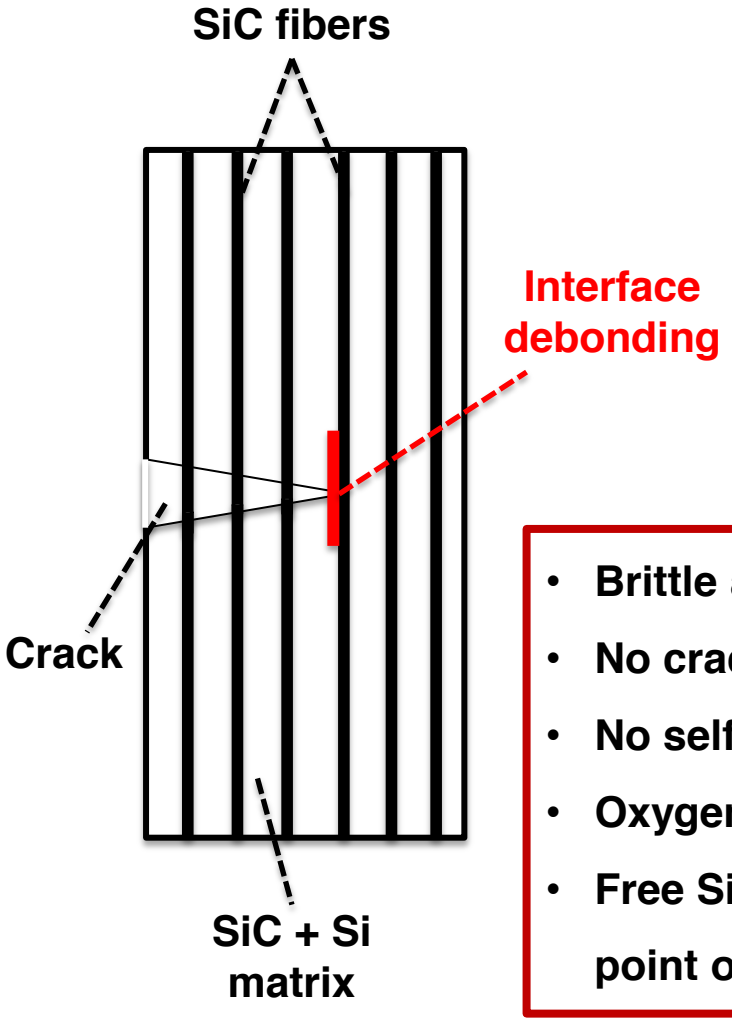
(Courtesy M. Singh)





Density ~ 96-97 %

Current SiC/SiC CMC Matrix Capabilities



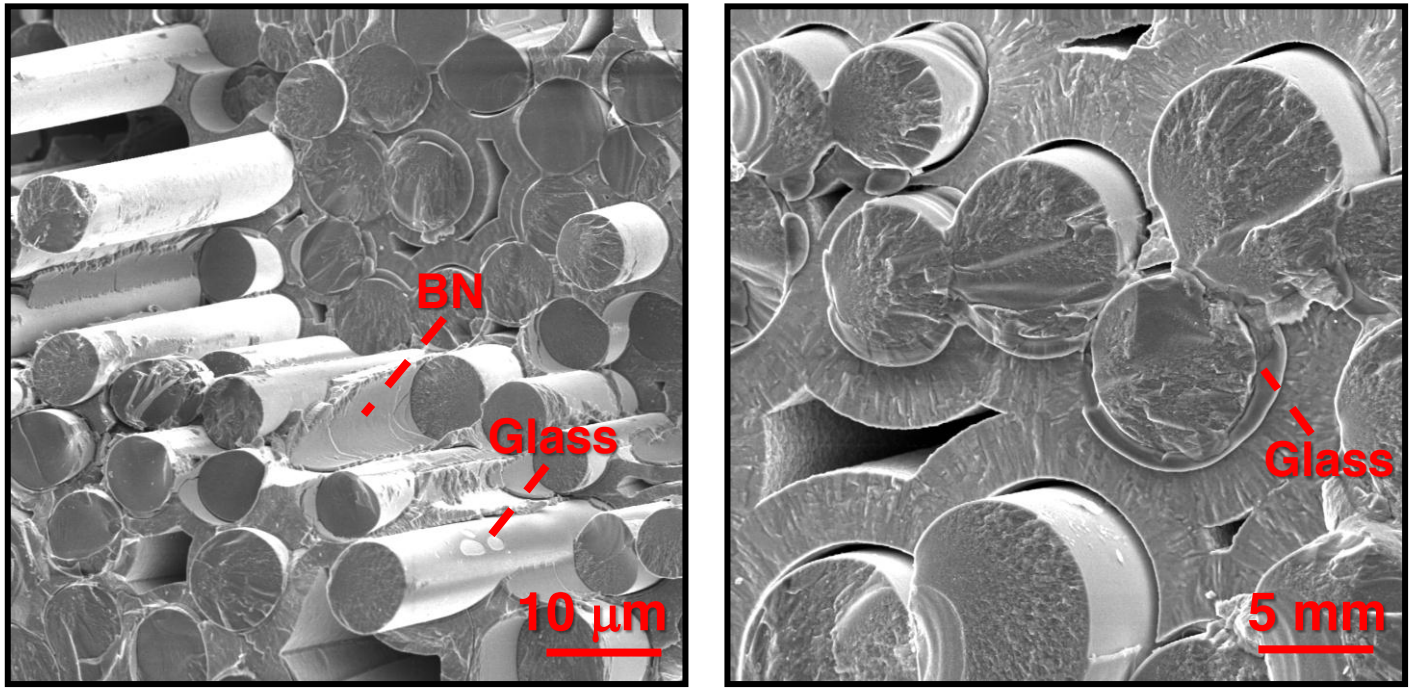
- Matrix fills space and provides a thermally conductive path.
- Fracture toughness due to crack bridging and interface debonding.
- Relatively low matrix cracking strength - $\sigma_{design} < \sigma_{proportional\ limit}$

- Brittle at all temperatures.
- No crack tip blunting – fast crack propagation.
- No self-healing.
- Oxygen ingress to the fiber coatings shortens fiber life.
- Free Si in the matrix limits temperature usage (melting point of Si: 1687 K; 1414 ºC; 2577 ºF).

Recession of BN and Formation of Glassy Phase in BN-Coated Hi-Nicalon MI SiC Composites

(Courtesy M. Singh)

T = 973 K; σ = 250 MPa;1000 h in air



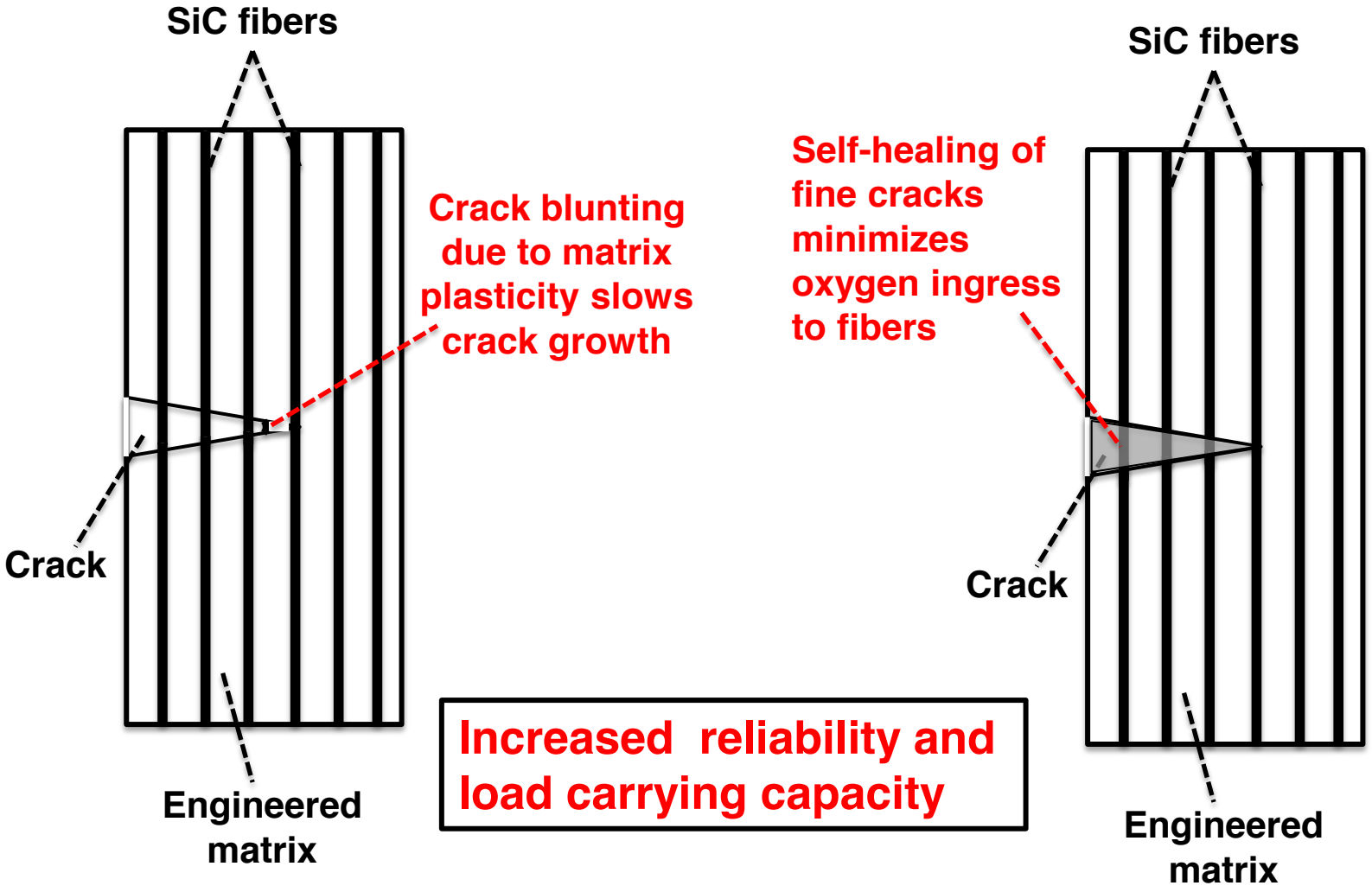
$$2BN\ (s) + 3/2\ O_2\ (g) = B_2O_3\ (l) + N_2\ (g)$$

B_2O_3 - SiO_2: Low eutectic temperature of 372 °C

Important Question

Can the matrix constituents be suitably engineered to develop a new generation of Engineered Matrix (Ceramic) Composites (EMCs) with improved properties and tailored for a specific component?

Crack Tip Blunting and Self-Healing



Increased reliability and load carrying capacity

Innovation and Expected Impact

- **High temperature matrix -** greater than 1589 K (1315 ºC/2400 ºF)
- **Matrix plasticity -** increased reliability, compliant matrix.
- **Chemical and thermal strain compatibility** with the coated SiC fibers.
- **Self-healing matrix -** prevents or minimizes oxygen ingress.
- **Low free Si -** reduces fiber attack, reduces incipient melting, increased high temperature capability.
- **Dense matrix -** high thermal conductivity.

Historical Perspective

Monolithic ceramics	Ceramic matrix composites (CMCs)	Engineered matrix composites (EMCs)
Low toughness Low strength	Higher toughness Higher strength Free silicon	Crack blunting & self-healing Low free silicon Higher toughness Higher strength Higher temperature

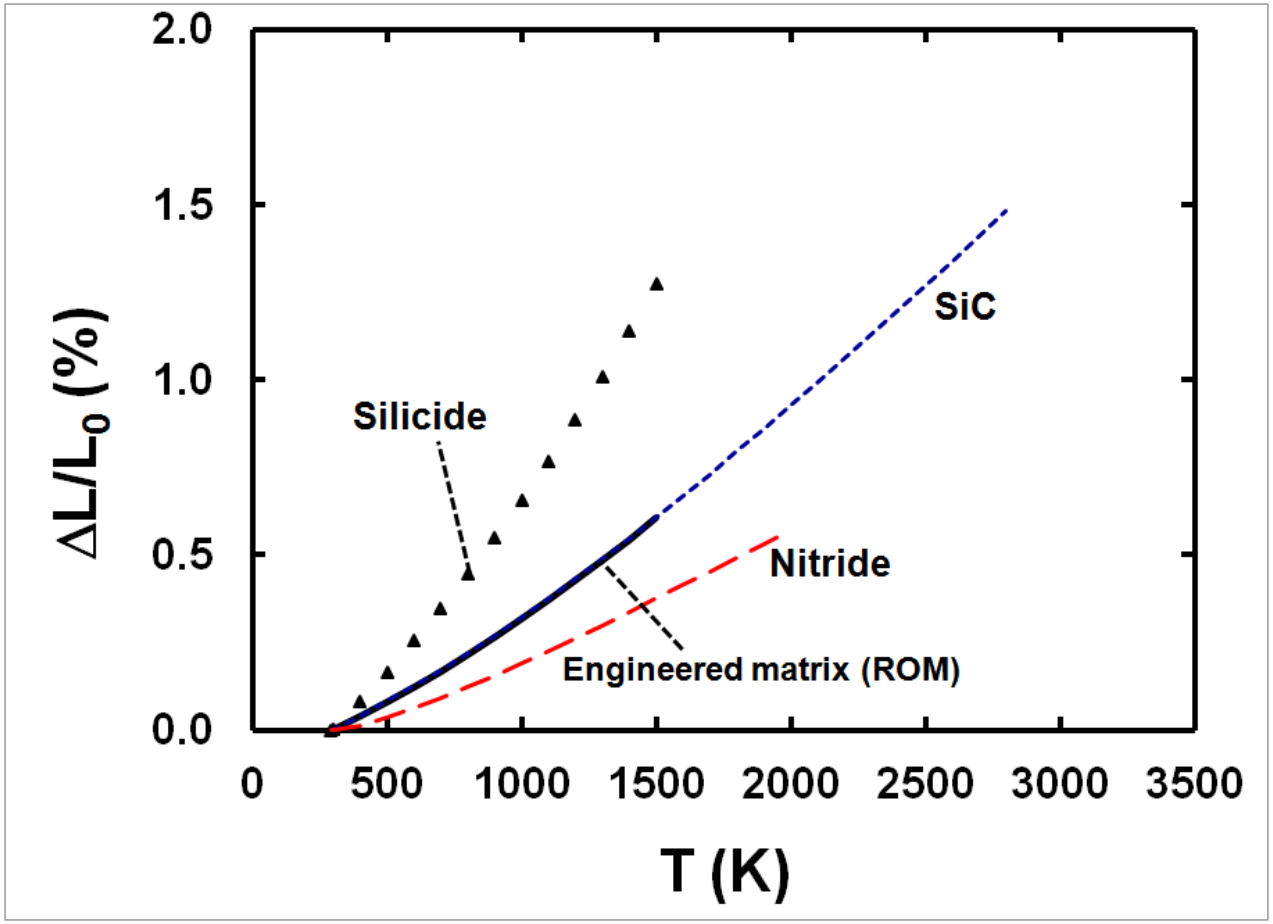
Technical Approach

- **Plasticity** – Introduce a chemically stable metallic silicide.
- **Temperature capability** – Choose silicides with melting points higher than that of Si (m.p. 1687 K; 1414 ºC; 2577 ºF).
- **Thermal expansion** – Match thermal expansion of the engineered matrix (EM) with the SiC fibers.
- **Self-healing capability** – Add constituents to heal cracks with low viscosity oxides or silicates.
- **Low Si** – Melt infiltrate with silicide instead of Si.
- **Dense EMCs** – Slurry infiltration and melt infiltration.

Silicide Additives

- $CrSi_2$
- $MoSi_2$
- $TiSi_2$
- WSi_2
- CrMoSi alloy

Matching Thermal Strains: Theoretical Concept



Matrix Design Concept

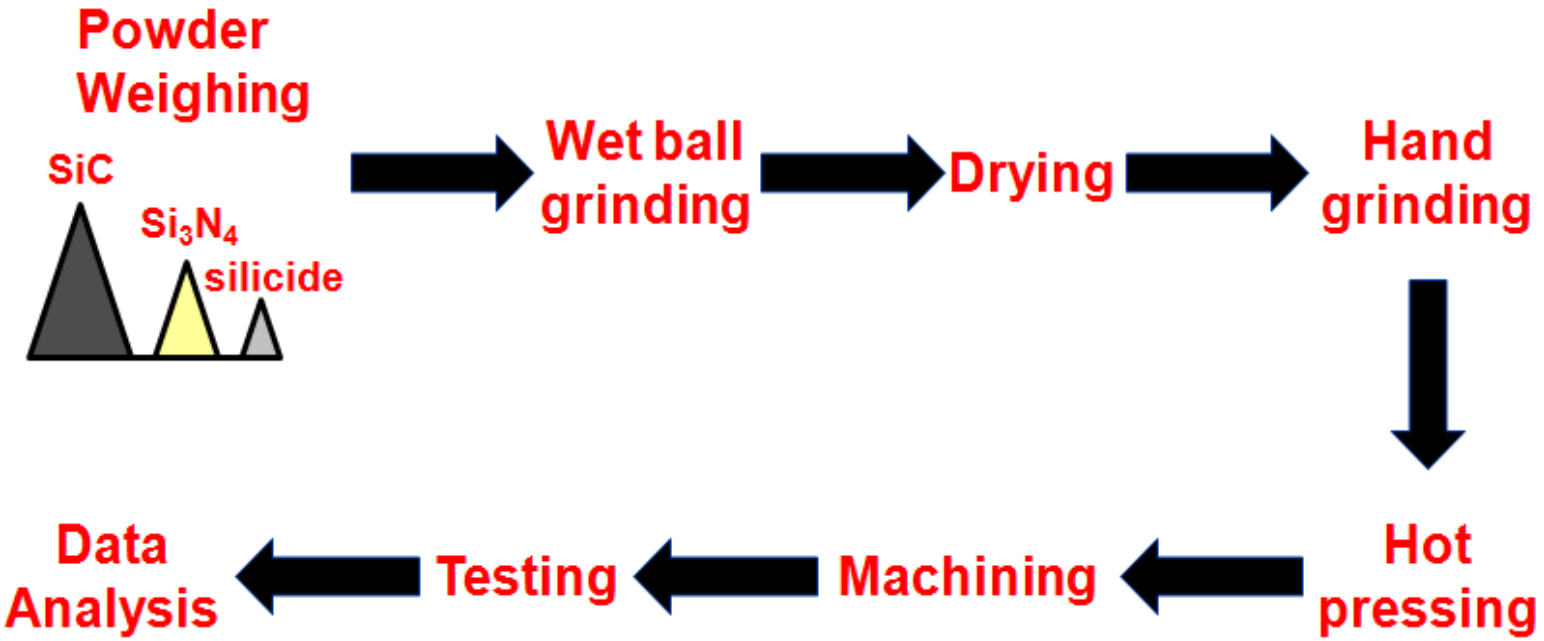
$$(\Delta L/L_0)_{fiber} = (\Delta L/L_0)_{EM} = V_{silicide}(\Delta L/L_0)_{silicide} + V_{SiC}(\Delta L/L_0)_{SiC} + V_{Si3N4}(\Delta L/L_0)_{Si3N4}$$

Concept	$V_{silicide}$ (%)	V_{SiC} (%)	V_{Si3N4} (%)
Traditional	0	100	0
Present investigation	x	(100-x-y)	y

Objectives

- Evaluate different engineered matrices based on theoretical concepts.
- **Proof of concept:** Demonstrate thermal strain compatibility with SiC.
- Evaluate bend and oxidation properties.
- Evaluate self-healing compositions.
- Fabricate and test engineered matrix composites.

Matrix Processing Steps

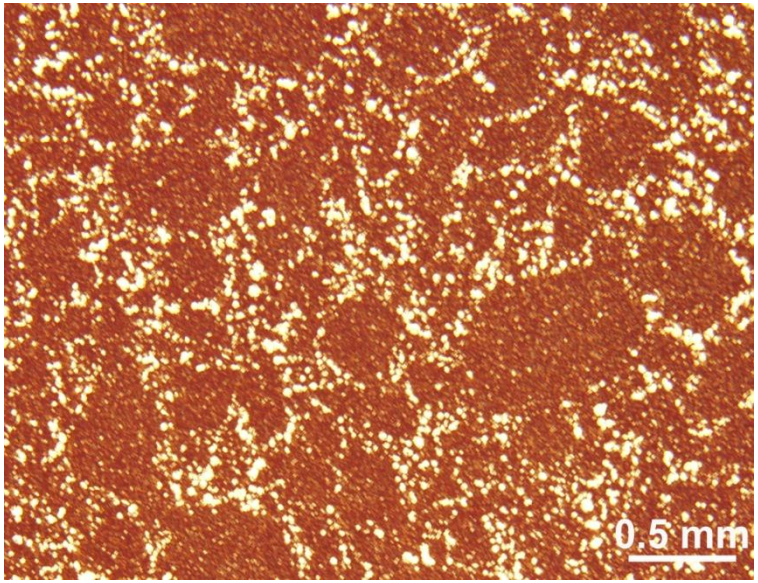


Hot-Pressed Plate and Optical Micrograph

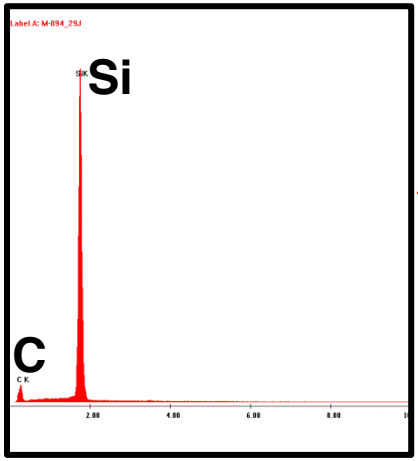
$CrMoSi/SiC/Si_3N_4$ (CrMoSi-EM)

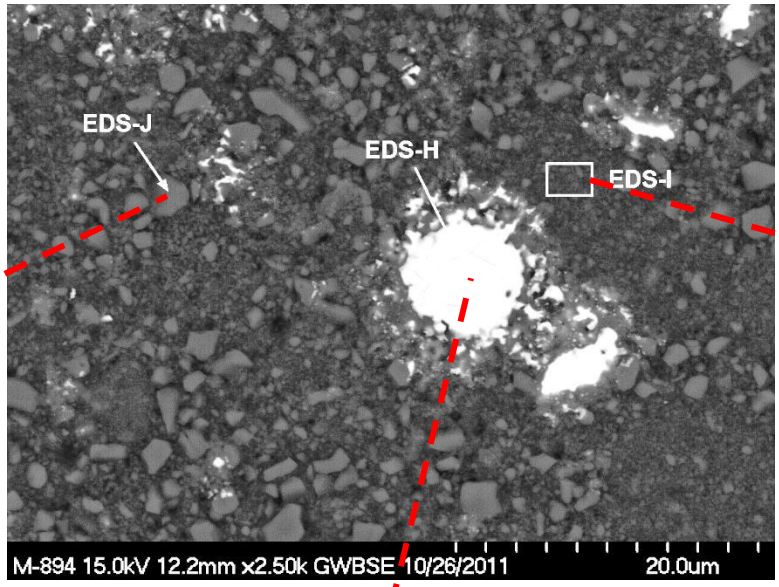
50 x 50 x 4 mm

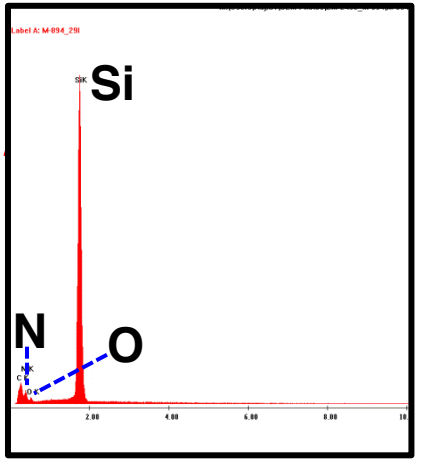
Optical micrograph

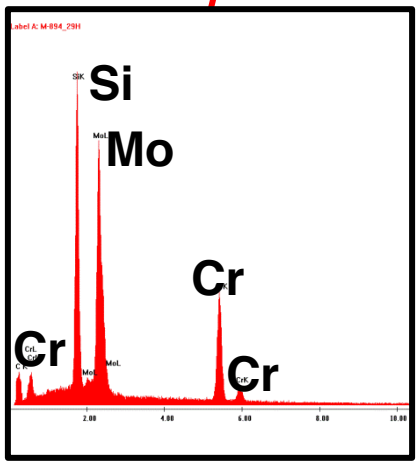


Back Scattered Image and Energy Dispersion Spectra: CrMoSi/SiC/Si_3N_4 (CrMoSi-EM)

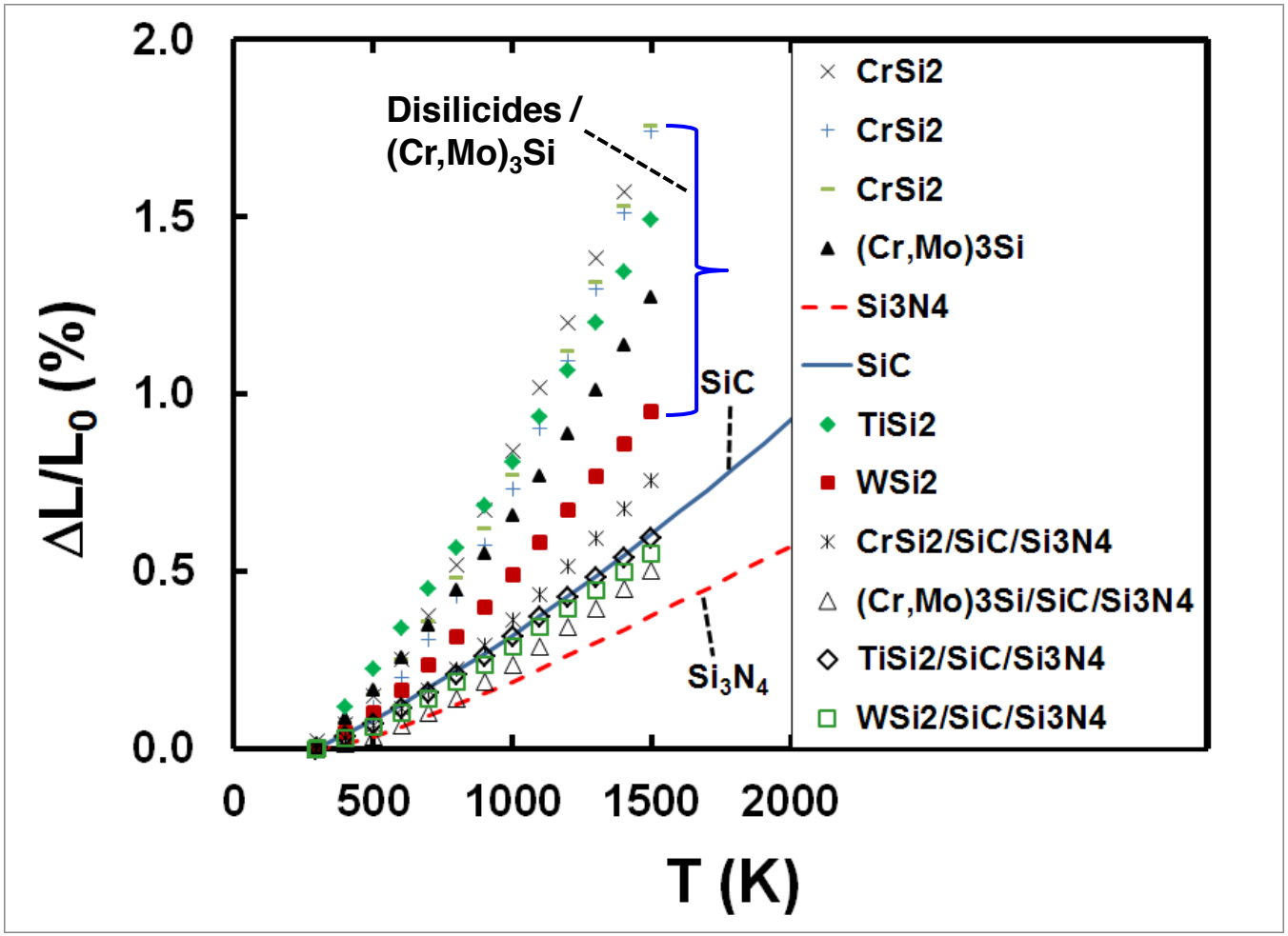




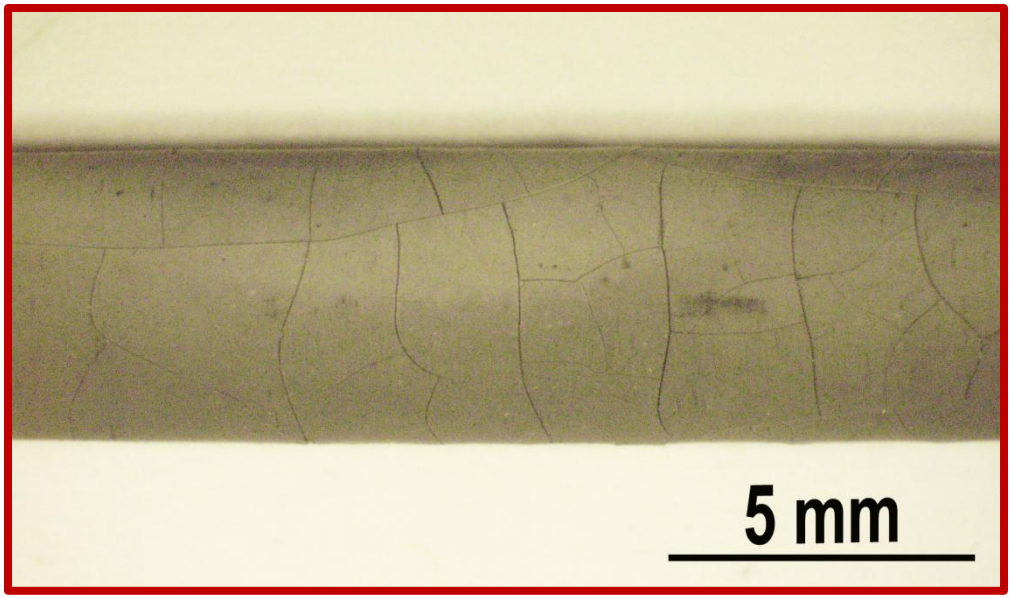




Proof-of-Concept: Thermal Strains

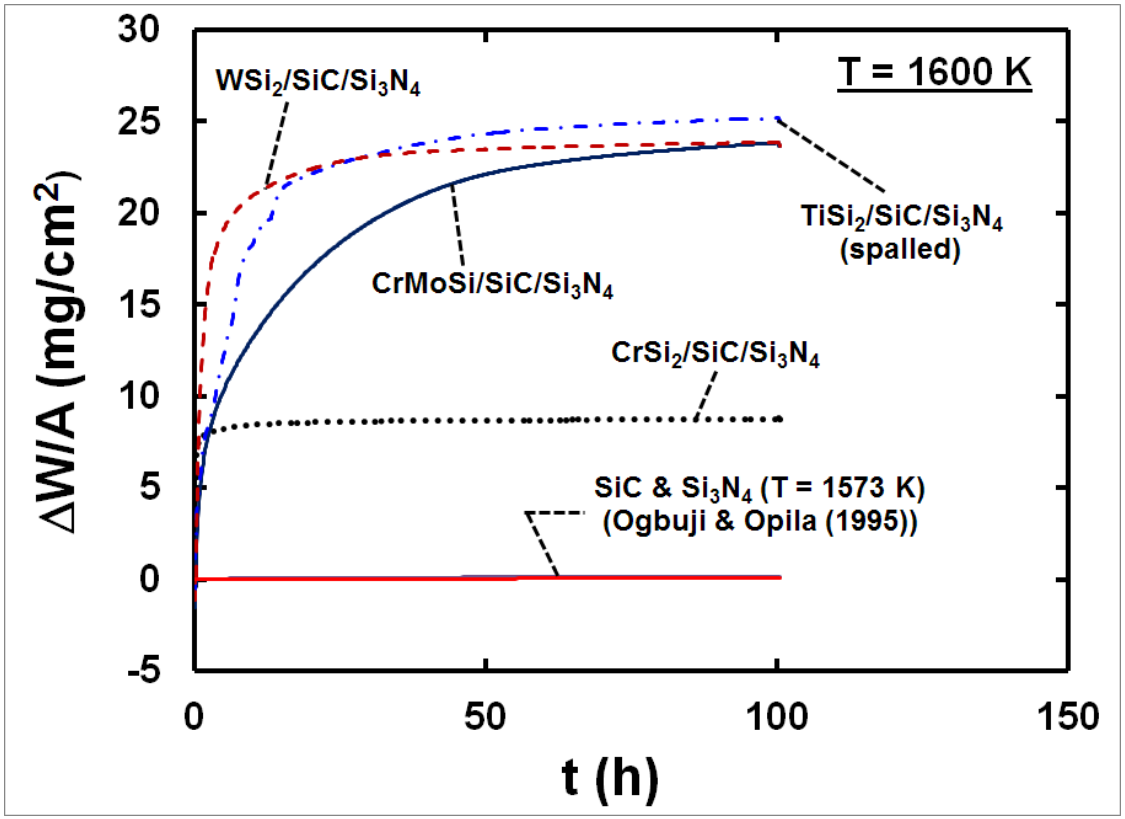


Macrograph of the Surface of a Thermally Cycled CTE $MoSi_2/SiC/Si_3N_4$ Specimen



- $MoSi_2/SiC/Si_3N_4$ engineered matrix dropped from the program.

Isothermal Oxidation Behavior of Engineered Matrices



$TiSi_2/SiC/Si_3N_4$ and $WSi_2/SiC/Si_3N_4$ engineered matrices dropped from the program

Four-Point Bend Stress-Strain Curves for a $CrSi_2$ Engineered Matrix

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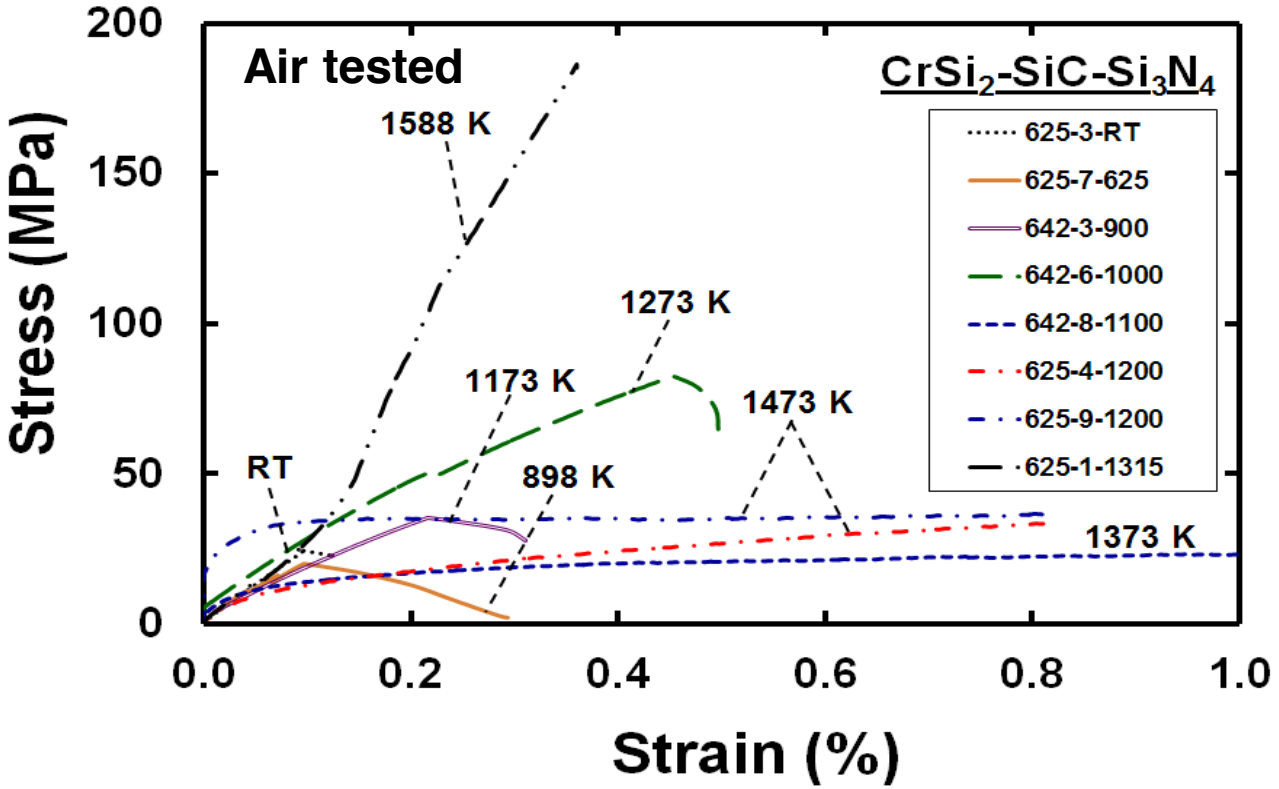
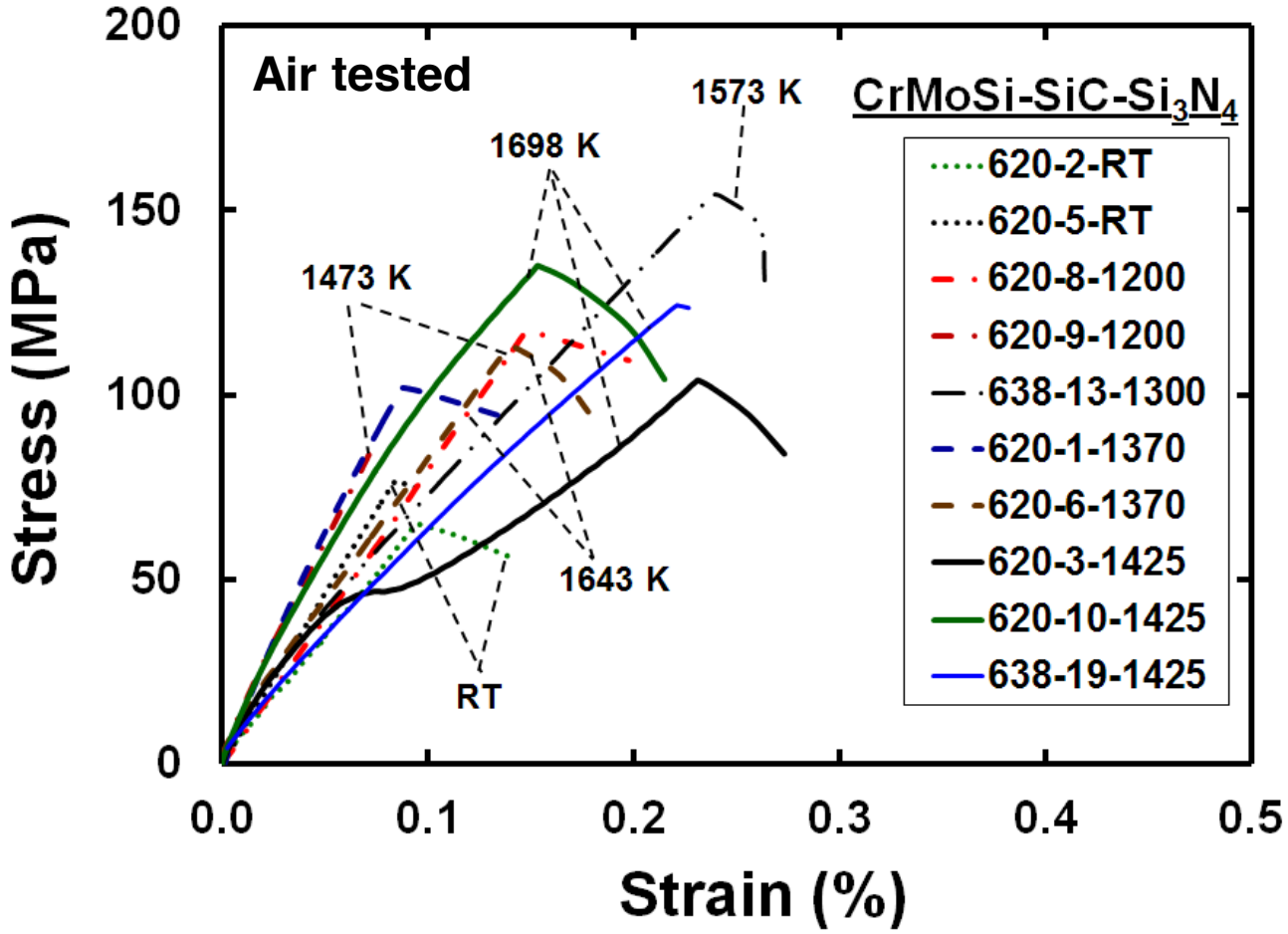
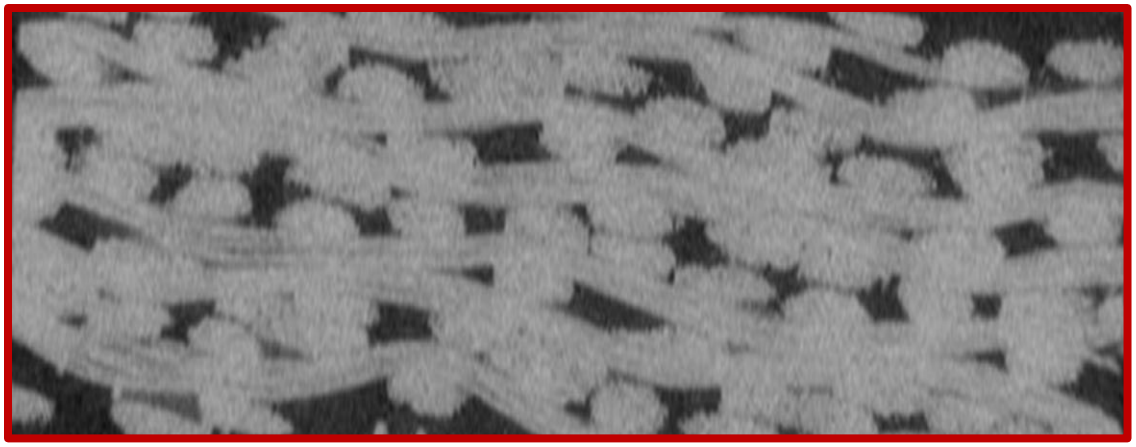


- Crack blunting due to crack tip plasticity increases bend strength

Four-Point Bend Stress-Strain Curves for a CrMoSi Engineered Matrix



CT Scan and a Schematic of the BN-Coated SiC/SiC Preform

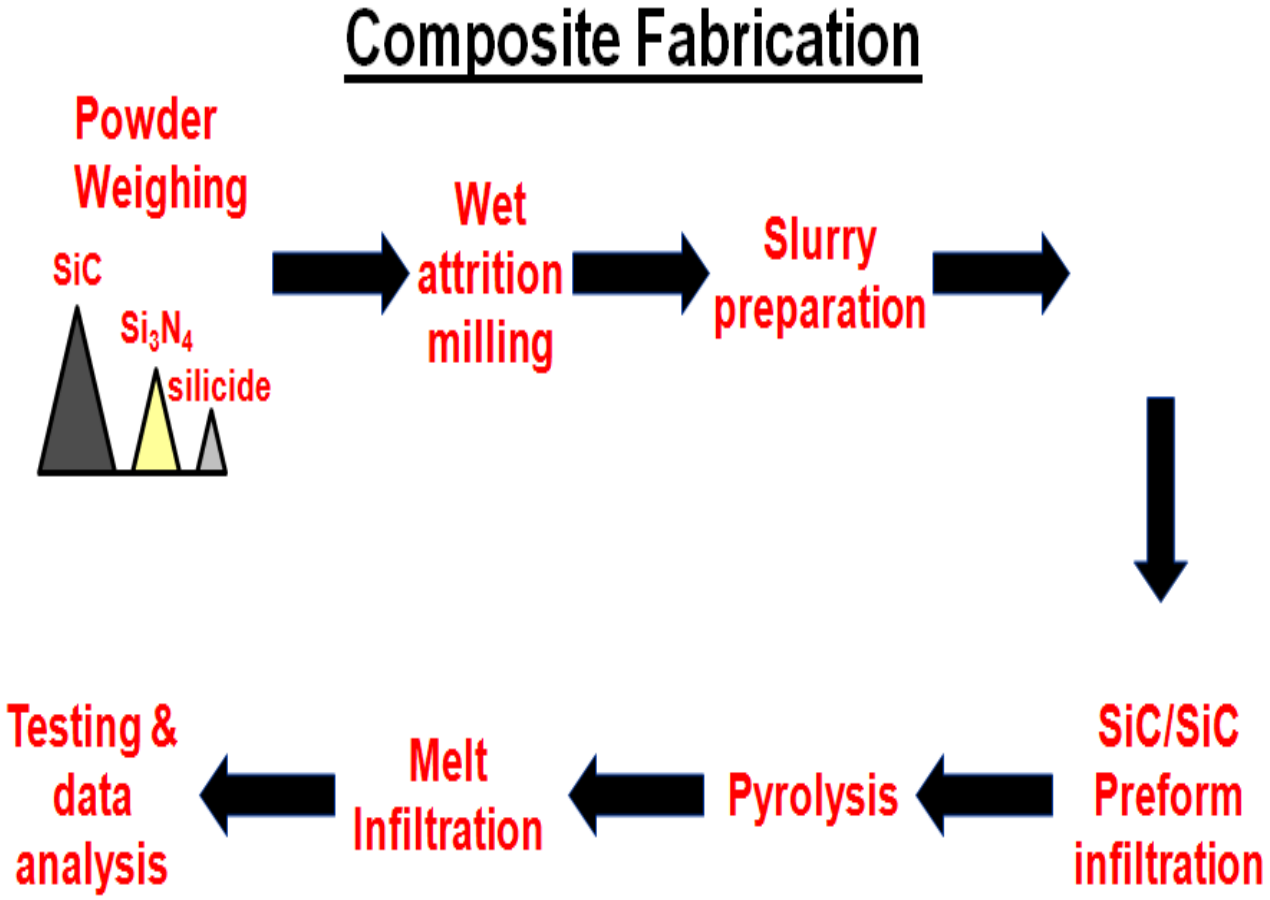


CT Scan

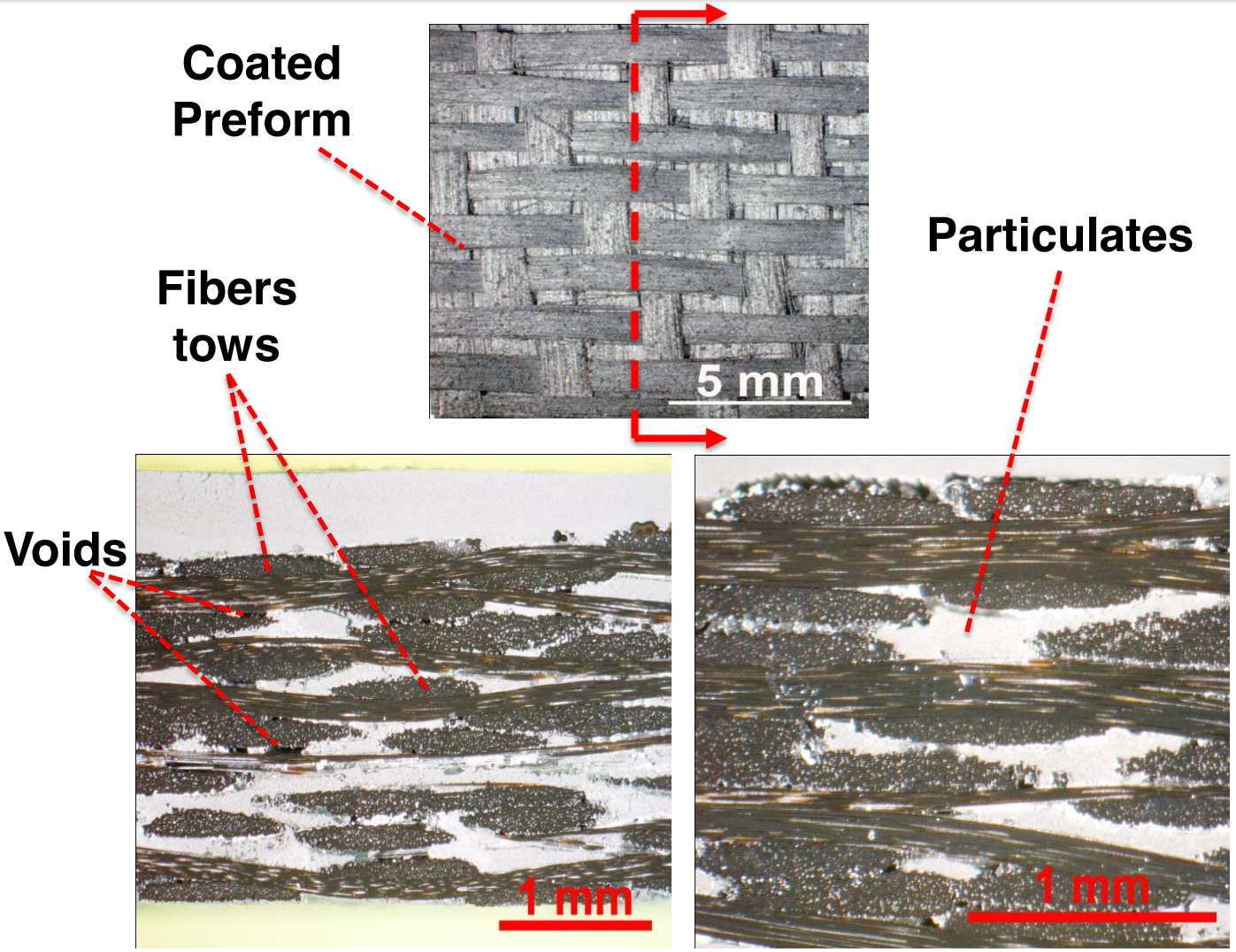
Schematic of void distribution

Void volume fraction ~ 25%

Steps in Engineered Matrix Composite Fabrication



Microstructures of $TiSi_2$-EM-Infiltrated SiC Fiber Preform



CT Scans of $TiSi_2/SiC/Si_3N_4$ Particulate Epoxy and Si- Melt Infiltrated Preform

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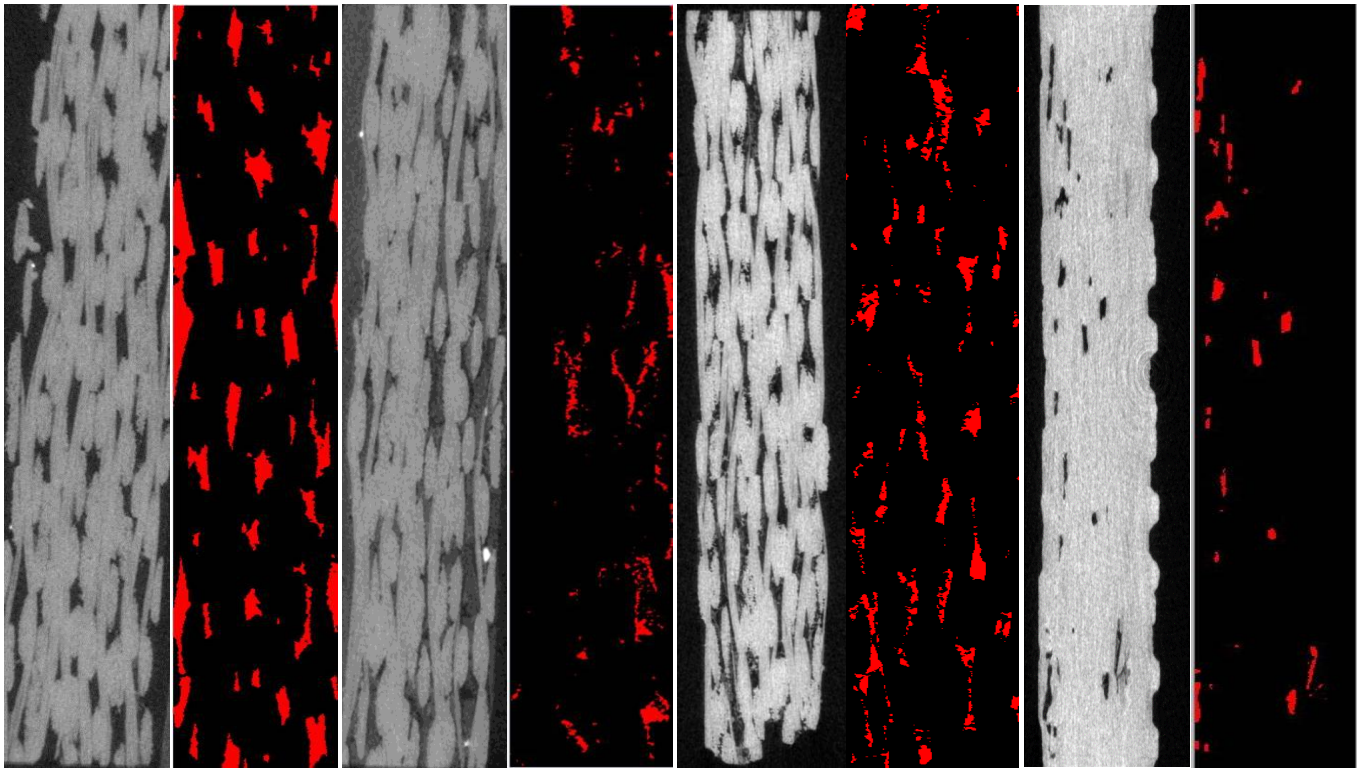
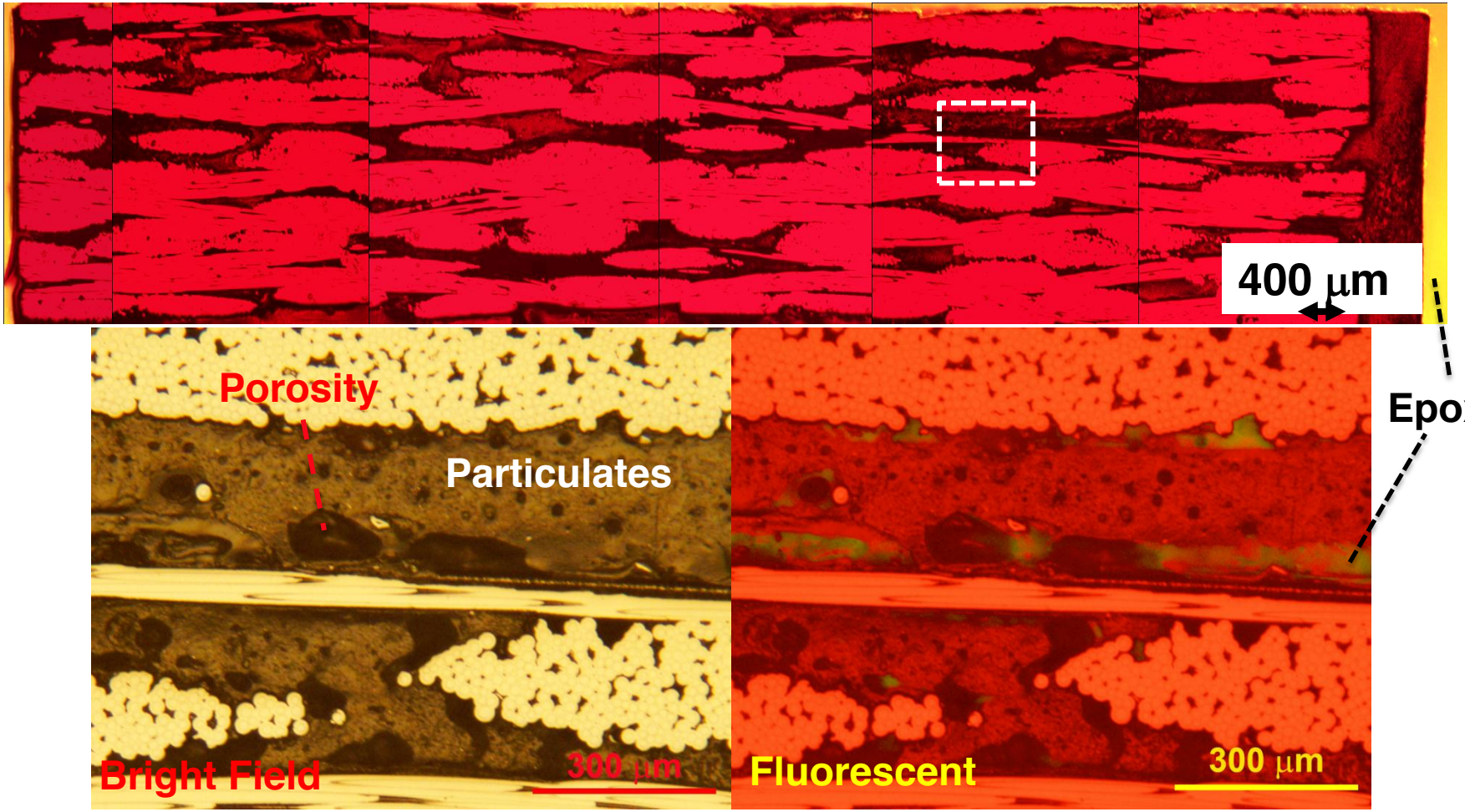
As-received Preform	Particulate Infiltrated	Pyrolized	Si Melt Infiltrated



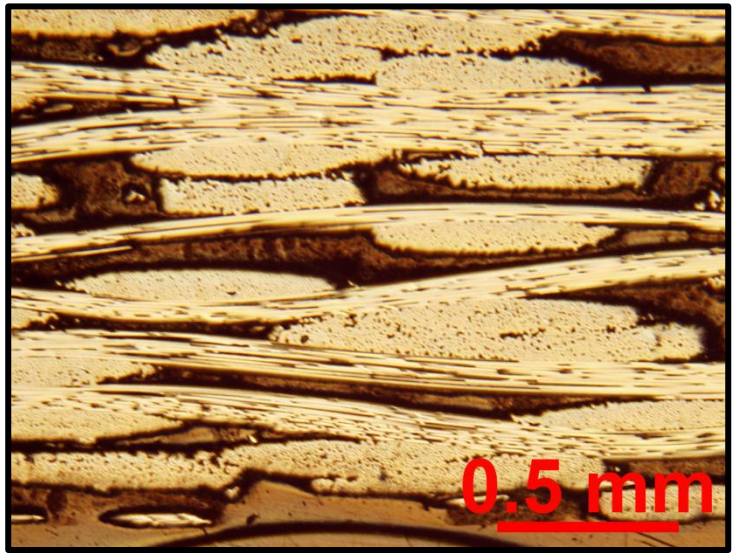
Area fraction of porosity ~ 21-23%	Area fraction of porosity ~ 0.9%	Area fraction of porosity ~ 6.6%	Area fraction of porosity ~ 1.8%

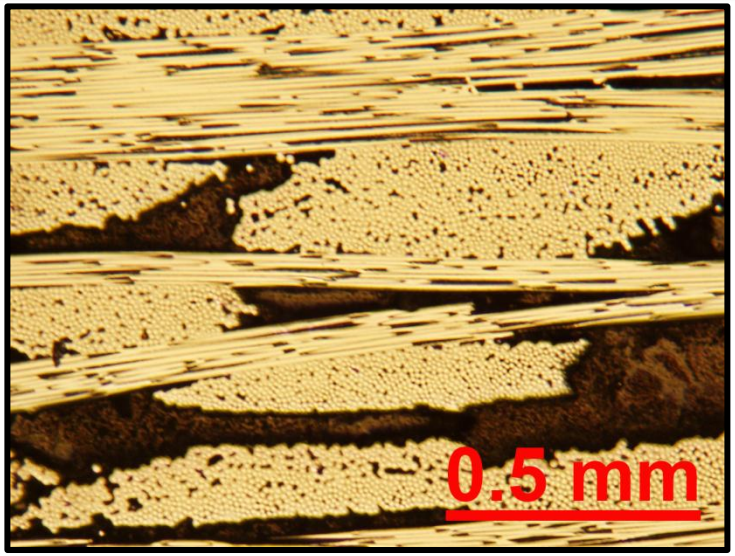
The red regions are voids

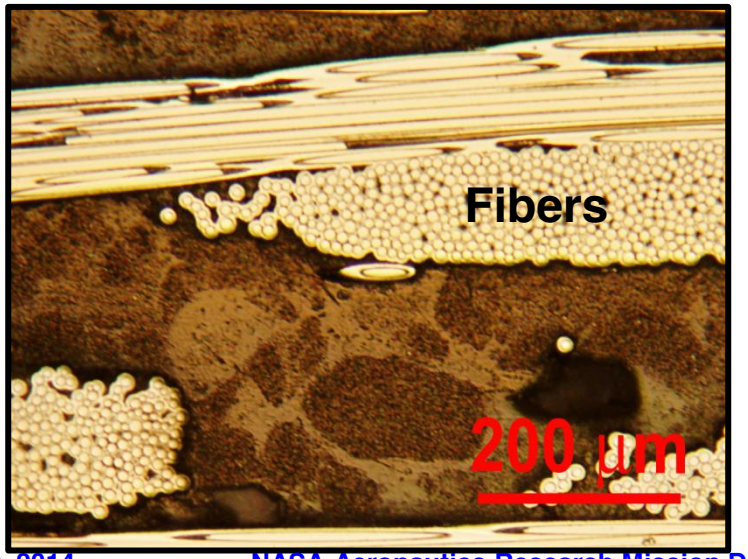
$TiSi_2/SiC/Si_3N_4$ epoxy infiltrated preforms

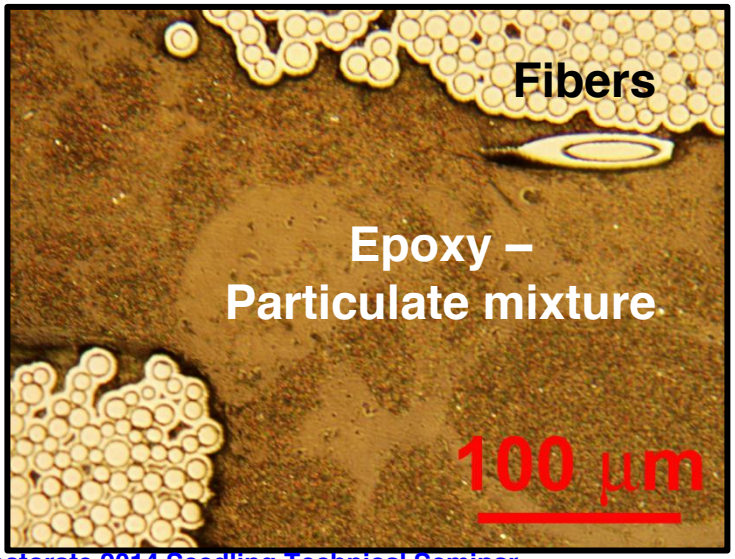


CrMoSi/SiC/Si_3N_4 Epoxy Infiltrated Preforms

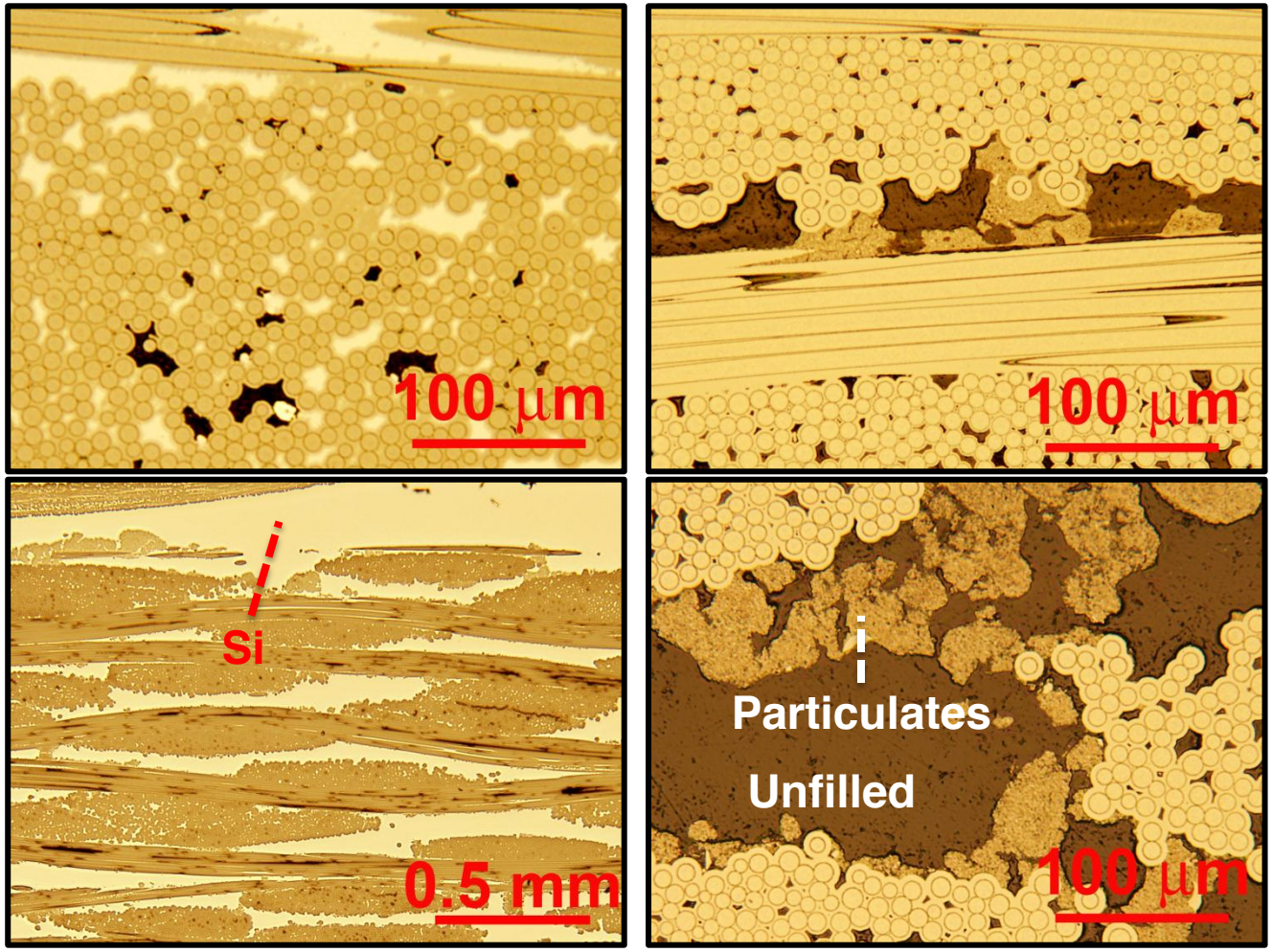




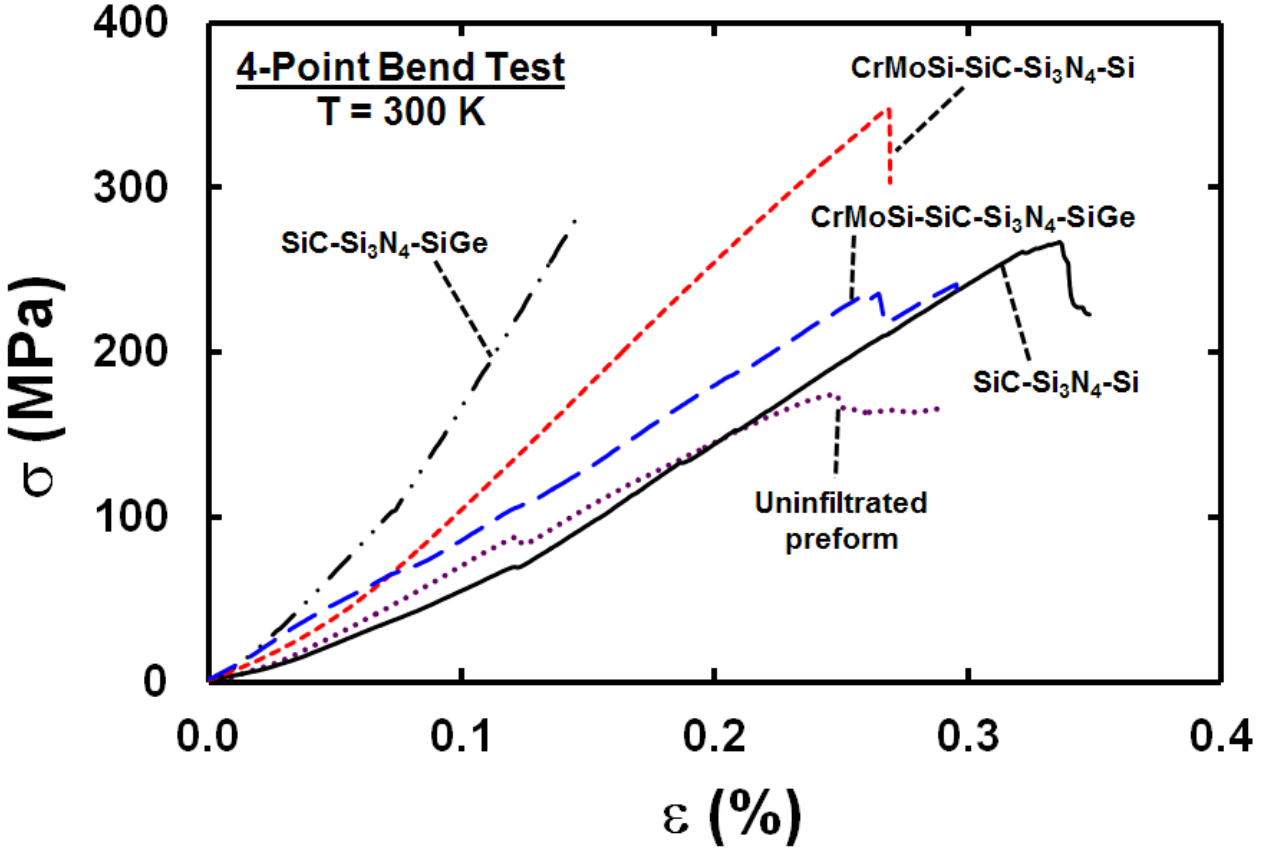




Particulate and Silicon Melt Infiltrated SiC/SiC Preforms

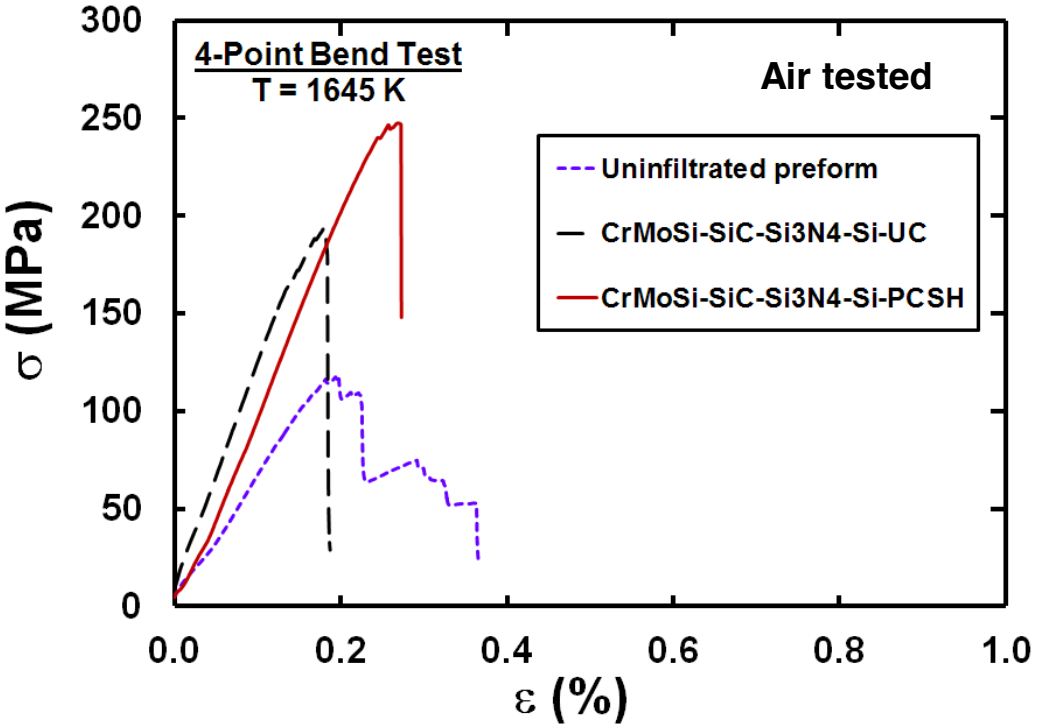


Room Temperature Bend Stress-Strain Curves for CrMoSi EMCs



Preliminary Studies:
Bend Strengths of CrMoSi-SiC-Si_3N_4-Si EMCs

Heat treated in air at 1600 K for 50 h



Assessment of the Self-Healing Characteristics of Different Additives to CrMoSi-SiC at 1600 K

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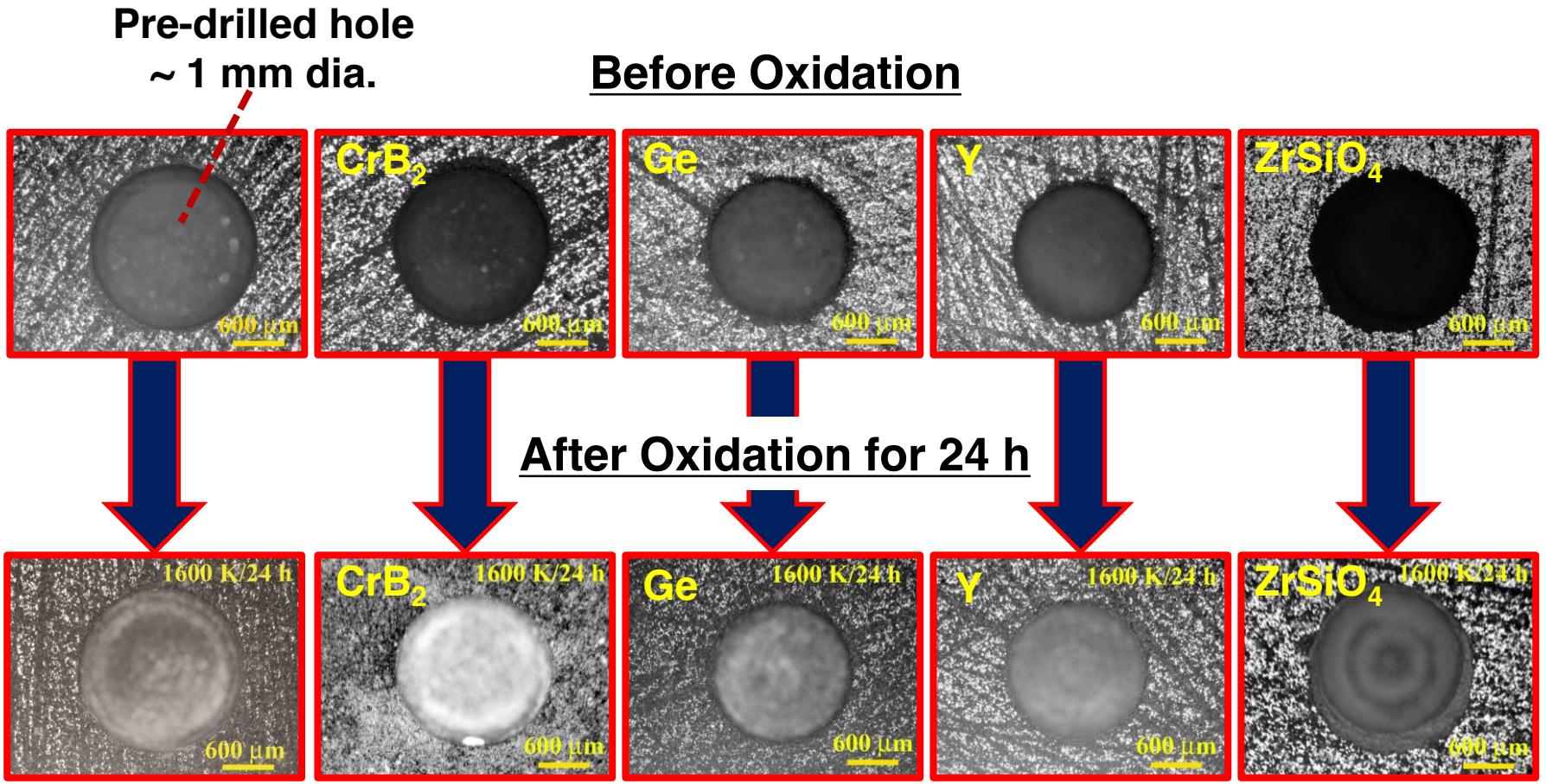

- CrB_2 addition shows the best ability to heal scratches

Self-Healing of CrMoSi-SiC with 5%CrB_2 at 1700 K after 100 h

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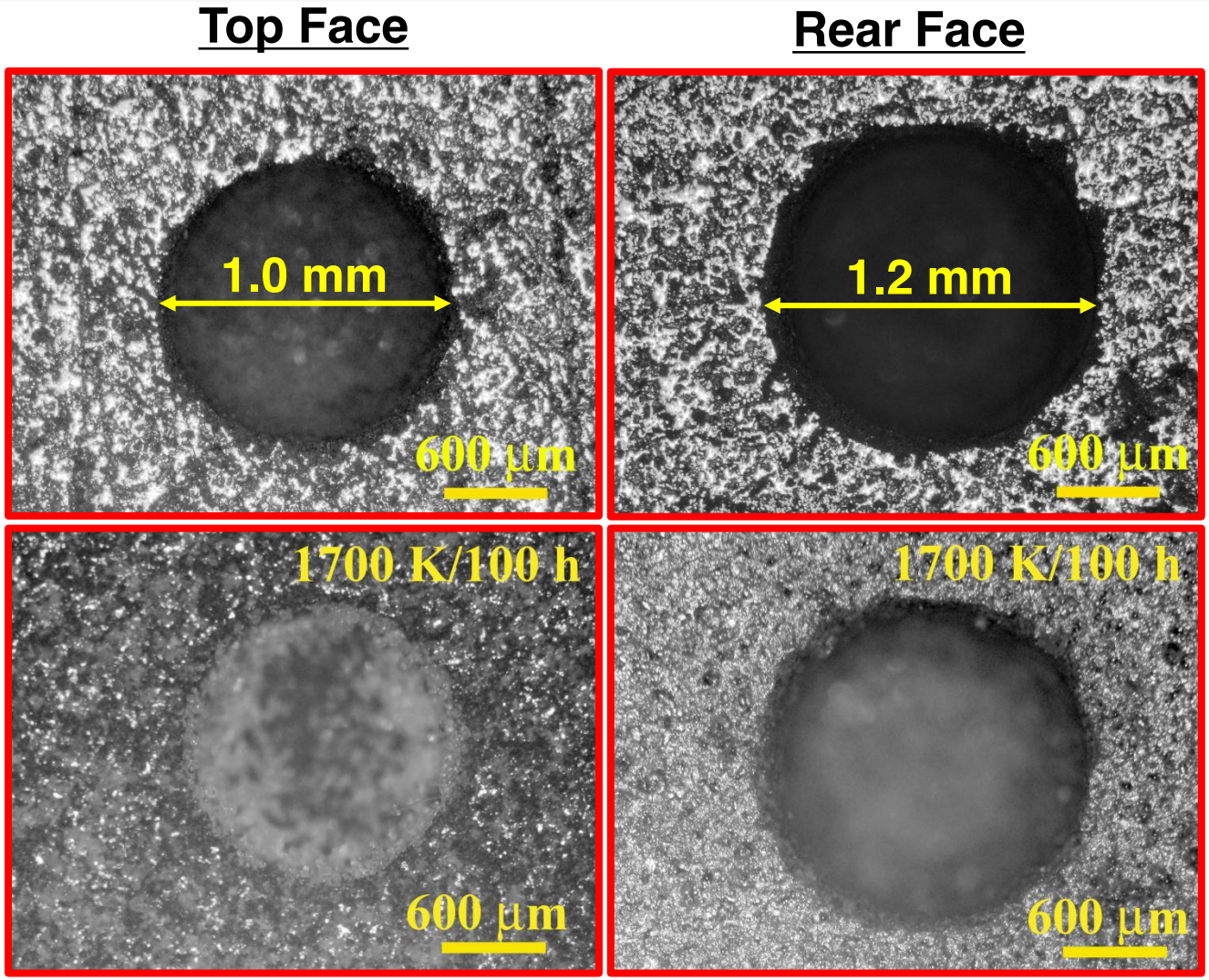

Self-Healing Characteristics of CrMoSi-SiC-CrB_2 Oxidized at 1700 K for 100 h

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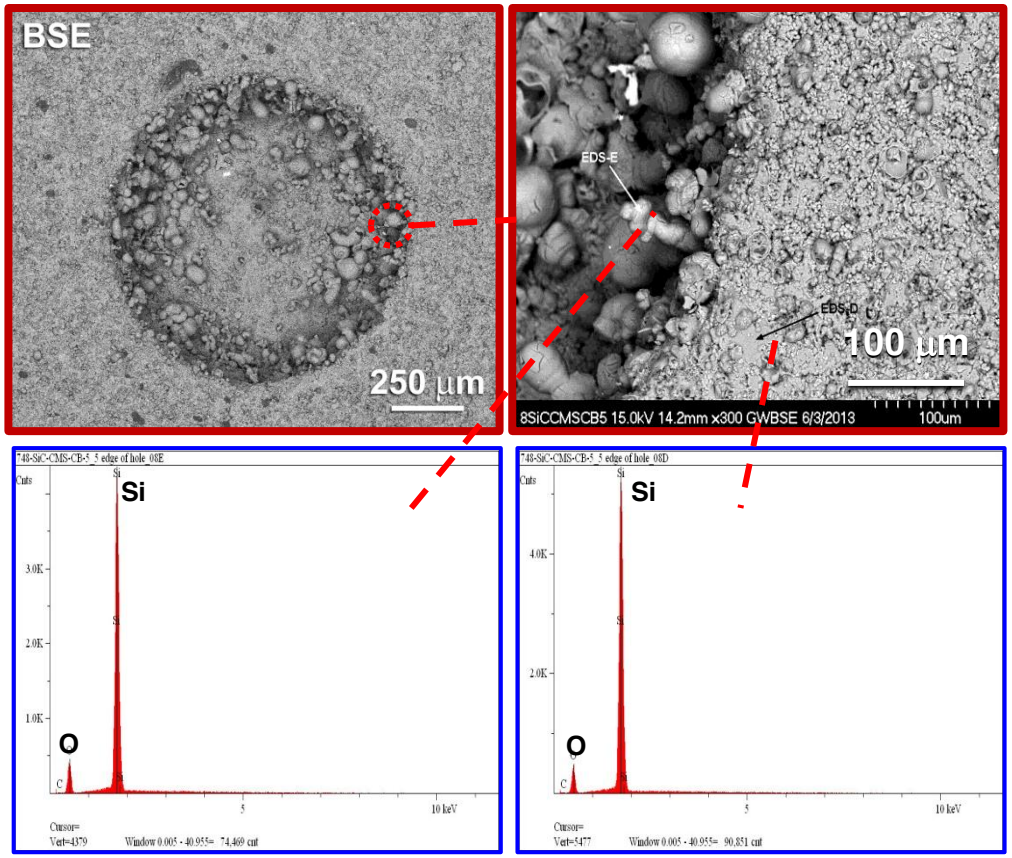

Summary and Conclusions

- **A concept for developing a new class of high temperature engineered matrix composites (EMCs) with crack blunting, self-healing and low Si capabilities using intermetallic silicides is proposed.**
- **The following concepts have been demonstrated:**
  - **Thermal expansion of the engineered matrix can be matched with that of SiC.**
  - **Increased matrix ductility can lead to higher bend strengths due crack blunting.**
  - **Promising self-healing additives have been identified.**
  - **$CrSi_2$/SiC/Si_3N_4 and CrMoSi/SiC/Si_3N_4 engineered matrices have been identified for 1589 K (2400 °F) and 1755 K (2700 °F).**
- **Several new compositions have been formulated for further studies.**
- **Fabrication of dense EMCs has proved to be challenging due to insufficient particle infiltration in the coated SiC/SiC woven preforms and due to poor capillarity action of the silcide alloys.**

Distribution and Dissemination

- **Applied for US Patent (May 30, 2013) –NASA Docket No: LEW 18964-1**

  Title: Engineered Matrix Self-Healing Composites

  S/N: 13/905,333; Filed: 5/30/13

  Inventors: Sai Raj, Mrityunjay Singh, Ramakrishna Bhatt

- **S. V. Raj, M. Singh and R. Bhatt, "High-Temperature, Lightweight, Self-Healing Ceramic Composites for Aircraft Engine Applications", NASA Tech Briefs, vol. 37, No. 2, p. 40 February 2013; http://www.techbriefs.com/component/content/article/5-ntb/tech-briefs/materials/15663-lew-18964-1.**

- **S. V. Raj, M. Singh and R. Bhatt, "Preliminary Studies on the Development of Engineered Matrices for SiC Fiber-Reinforced Ceramic Composites", 38th Annual Conference on Composites, Materials and Structures, Cocoa Beach, FL Jan 26-30, 2014**

- **Journal paper submitted for DAA 1676 management approval.**

Next Steps

- The research has been transferred to ARMD's Aero Sciences Program (FY 14).
- Methods to increase particulate loading and silicide melt infiltration of the preforms are being studied.
- Dynamic fracture toughness tests are underway to quantify the self-healing capabilities of several engineered matrices.
- Bend and tensile creep tests of several engineered matrix specimens are planned.
- Final ARMD report.